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SOLVENT EFFECTS ON SEVERAL POLYMERIZATIONS UNDER HIGH PRESSURE

BY YOSHIAKI OGO AND TATSUYA IMOTO

As one of investigations about the effects of solvent on chemical reactions under high pressure, some polymerizations and copolymerizations in solution were studied under the pressure up to 4,000 kg/cm². In the polymerization of vinylacetate, the chain transfer to solvent was influenced with the pressure. At the polymerization of itaconic acid, a new phenomenon named as critical pressure of polymerization was found which showed various values referring to the solvents used.

Also, the polymerization of vinylchloride was carried out under high pressure and the polymers having isotactic crystallinity were obtained.

As for the copolymerization, both vinylchloride and crotonaldehyde were copolymerized with various olefinic monomers, and the progressive effect of the pressure would be appeared for the conjugated monomers participated. And the difficulties or easiness of these copolymerization were compared under high pressures.

Introduction

There have been many studies on the solvent effects on various reactions under high pressure. One of the most fruitful result obtained on this problem is the electrostriction theory owing to Hamann and his collaborates¹⁾. In general, in the case of reaction in solution there occurs some extent of volume contraction through the solvation of solvent molecules, especially electrostriction when the activated complex is more polar than the reactant molecule. And this contraction does accelerate the reaction under high pressure.

On the other hand, among many sorts of reactions polymerization reaction, whatever kind it may be, is considerably accelerated by pressure in virtue of the volume contraction. Standing on these points, we have been studying the polymerization and copolymerization of various compounds under high pressure and in solution²⁾⁻⁸⁾.

In the following, some results obtained on the polymerization of vinylacetate (VAc), itaconic acid (IA), and vinylchloride (VC) and the copolymerization of crotonaldehyde and VC, respectively, with

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- 1) S. D. Hamann, "Physico-Chemical Effects of Pressure", Butterworth Scientific Pub., London (1957)
- 2) T. Imoto and T. Matsubara, *J. Polymer Sci.*, **56**, 54 (1962)
- 3) T. Imoto and T. Matsubara, *ibid.*, **A2**, 4573 (1964)
- 4) T. Imoto, K. Aotani, T. Kojima and N. Makino, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **87**, 1149 (1966)
- 5) T. Imoto and T. Nakajima, *Kogyo Kagaku Zasshi (J. Chem. Japan, Ind. Chem. Sect.)*, **69**, 520 (1966)
- 6) H. Asai and T. Imoto, *Polymer Letter*, **2**, 553 (1964)
- 7) T. Imoto, T. Oota and J. Kanbara, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **82**, 378, 492 (1961)
- 8) M. Ooiwa, T. Matsubara and T. Imoto, *ibid.*, **84**, 387 (1963)

other vinyl compounds will be reported.

However, it may be noticed that for the sake of simplicity only results and discussion without experimentals will be described in this paper.

Polymerization of Vinylacetate⁹⁾

In the polymerization of VAc, it is recognized that chain transfer reaction to solvent molecule happens always simultaneously¹⁰⁾. The pressure effect on the chain transfer reaction by the polymerization of styrene to solvents has been studied by Walling¹¹⁾ and Weale¹²⁾. Walling and Pellon¹³⁾ determined the solvent transfer constant ($C_s = k_{tr}/k_p$) for styrene with carbon tetrachloride at various pressure and 60°C. They found that C_s is reduced by only about 15 per cent at 4,000 kg/cm², so that the rate of solvent transfer in this system is accelerated by pressure to nearly the same extent as that of chain propagation. They estimated ΔV_{tr}^* , the activation volume of chain transfer between polystyryl radical and carbon tetrachloride, to be -11.0 ml/mole from the results of Nicholson and Norrish¹⁴⁾.

However, solvent transfer constant for styrene with triethylamine was appreciably decreased at 4,400 kg/cm² according to the results of Weale and Toohey¹⁵⁾. Their activation volume of chain transfer, ΔV_{tr}^* , was only -2 or -3 ml/mole which was unexpectedly small.

In this study, chain transfer constants were determined by following Mayo's equation¹⁶⁾.

$$\frac{1}{P} = \frac{1}{P_0} + \frac{C_s[S]}{[M]} \quad (1)$$

where $[S]$ and $[M]$ are molar concentration of solvent and monomer, P and P_0 are degree of polymerization with and without solvent, respectively. On the other hand, chain transfer constant can be related to pressure by the following equation since this constant is given as the ratio of transfer rate constant to propagation rate constant, and using van't Hoff's relation,

$$\ln(C_s)_p = \ln(C_s)_1 + ap \quad (2)$$

where

$$a = -(\Delta V_{tr}^* - \Delta V_p^*)/RT \quad (3)$$

and ΔV_p^* is the activation volume referring to the transition state of chain growth.

According to equation (1), plots of $1/P$ vs. $[S]/[M]$ are shown in Figs. 1 and 2 in the case of chlorobenzene and bromobenzene. C_s values at each pressure obtained from the slopes of these lines and results with toluene are summarized in Table 1.

The magnitude of the chain transfer constants in this series is in following order,

chlorobenzene < bromobenzene < toluene

- 9) H. Nakamoto, Y. Ogo and T. Imoto, *Makromol. Chem.*, **111**, 93 (1968)
- 10) S. Okamura and T. Yamashita, *Kaken-Koenshū*, **18**, 46 (1946)
- 11) C. Walling and J. Pellon, *J. Am. Chem. Soc.*, **79**, 4776 (1957)
- 12) K. E. Weale, *Quart. Rev.*, **16**, 267 (1962)
- 13) C. Walling and J. Pellon, *J. Am. Chem. Soc.*, **79**, 4782 (1957)
- 14) A. E. Nicholson and R. G. W. Norrish, *Disc. Faraday Soc.*, **22**, 97, 104 (1956)
- 15) K. E. Weale and A. C. Toohey, *Trans. Faraday Soc.*, **58**, 2446 (1962)
- 16) F. M. Merrett and R. G. W. Norrish, *Proc. Roy. Soc.*, **206**, 309 (1951)

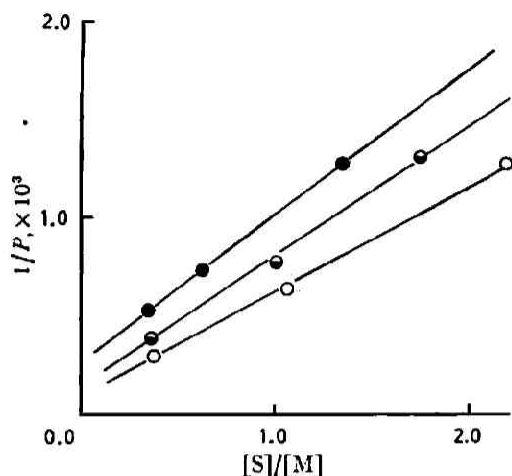


Fig. 1 Polymerization of vinylacetate in chlorobenzene (60°C)

—○— 2000 kg/cm², —◐— 1000 kg/cm²,
—●— 1 kg/cm²

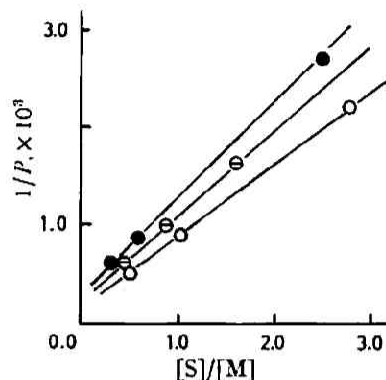


Fig. 2 Polymerization of vinylacetate in bromobenzene (60°C)

—○— 2000 kg/cm²,
—◐— 1000 kg/cm²,
—●— 1 kg/cm²

Table 1 The solvent transfer constants ($C_s \cdot 10^3$) at different pressures at 60°C

Solvent	Pressure (kg/cm ²)		
	1	1000	2000
-Cl	0.80	0.68	0.56
-Br	1.00	0.92	0.80
-CH ₃	6.90	4.90	—

The energy of carbon-halogen bond decreases with the increase of atomic radius of the halogen atom, which supports the higher value of C_s for bromobenzene than for chlorobenzene.

These C_s values are plotted by means of equation (2) in Fig. 3. The differences of activation volume between propagation and chain transfer reaction, ($\Delta V^*_{tr} - \Delta V^*_p$), are calculated from the slopes of these lines using equation (3) and summarized in Table 2.

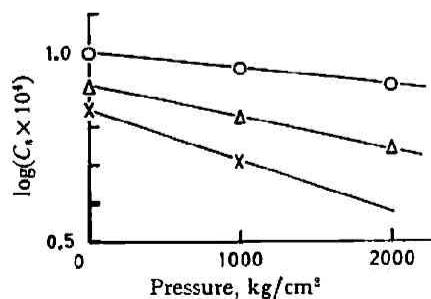


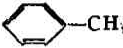
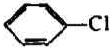

Fig. 3 Pressure dependence of solvent transfer constants (60°C)

—○— -Br, —△— -Cl,
—×— -CH₃

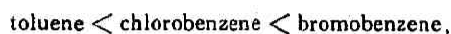
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Table 2 The variation of the differences of the activation volume with solvents

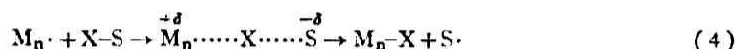
Solvent			
$\Delta V^*_{tr} - \Delta V^*_p$ (ml/mole)	9.4	5.0	2.8

The order of pressure dependence in the chain transfer on solvent in this series is in



since ΔV^*_p does not depend so much upon organic solvent.

A chain transfer reaction can be assumed to proceed through a formation of the following bimolecular transition state.



where $M_n \cdot$ and $X-S$ represent a growing radical and a solvent, respectively.

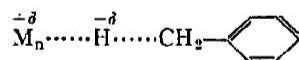
The effect of pressure on the chain transfer reaction as shown in equation (4) is strongly dependent on the radius of the atom abstracted, or on the polarity of the transition state. The bond distance of $S-X$ and the polarizability of the abstracted atom for some examples are tabulated in Table 3.

Table 3 Bond distance between $S-X$ and polarizability of the abstracted atom (X)

$S-X$	Bond distance (Å)	Polarizability (ml)
C-H	1.08	1.69
C-Cl	1.75	6.53
C-Br	1.91	9.37

From this table, as bromobenzene is larger than chlorobenzene with respect to bond distance and the polarizability, it is predicted that the former may be more pressure dependent than latter in the chain transfer reaction. This prediction could be confirmed practically by the values in Table 2.

On the other hand, the following transition state can be considered in the case of toluene and triethylamine.



From the value of the distance and polarizability of hydrogen atom, the effect of pressure on this transfer reaction could not be expected.

Polymerization of Itaconic Acid¹⁷⁾

It has been previously reported by many authors¹⁸⁾⁻²⁵⁾ that IA does not homopolymerize but

17) H. Nakamoto, Y. Ogo and T. Imoto, *Makromol. Chem.*, **111**, 104 (1968)

18) C. E. Schildknecht, "Vinyl and Related Polymers", John Wiley and Sons Inc., New York, (1952)

19) S. Nagai, *Science and Industry, Japan*, **36**, 76 (1962)

20) R. G. Fordyce and G. H. Ham, *J. Am. Chem. Soc.*, **69**, 695 (1947)

copolymerize with various compounds. In 1959 Marvel and Shepherd were the first to be successful in polymerizing IA in aqueous hydrochloric acid solution using potassium persulfate²⁶⁾ as catalyst. Subsequently Nagai and Yoshida²⁷⁾ also investigated the ionic polymerization of IA in aqueous solution. While, the polymerization of IA in organic solvents using radical initiator has not been reported until Braun and El Sayed²⁸⁾ polymerized the acid in dioxane in 1966; however, a long period (about several days) was required to obtain higher polymerization yield.

Standing on these facts we had tried to obtain polymer of IA by radical polymerization under high pressure and succeeded with considerable yield in short period. In the following, the effects of pressure and solvents will be described.

Some results of polymerization of IA in methanol solution using benzoyl peroxide as initiator are shown in Table 4.

Table 4 Polymerization of itaconic acid in methanol solution at 50°C

Pressure (kg/cm ²)	[I] (mole/l)	[M] (mole/l)	Polymn. time (hr)	Yield (%)
5,000	3.88×10^{-2}	0.96	5.0	43.4
1	3.88×10^{-2}	0.96	48	—
1	1.71×10^{-1}	1.46	24	—
5,000	1.71×10^{-1}	1.46	4.0	54
1,000	1.71×10^{-1}	1.46	5.5	—
1	1.71×10^{-1}	1.46	100	—

I: Benzoyl peroxide (BPO)

As can be seen in the table, under elevated pressure IA does polymerize in methanol. On the other hand, any attempts to polymerize under atmospheric conditions and/or with increased initiator and monomer concentrations were unsuccessful.

Sugihara and Yoda²⁹⁾ had made attempts to polymerize the acid, but in vain. Also in our experiment, the polyacid could not be obtained under atmospheric pressure in a hundred hours.

The effects of pressure on the polymerization yield in several organic solvents are shown in Fig. 4, in which polymerization time, monomer and initiator concentrations are constant as shown in the below. It is quite interesting that the polymerization in dioxane is most sensitive to pressure and moreover that a critical pressure exists for each solvent.

The polymerization mixtures in methanol and dimethylformamide (DMF) were homogeneous and in other solvents heterogeneous. The critical pressures which mean the lowest limit pressure to allow polymerization are tabulated in Table 5 together with dielectric constants of respective solvents and

21) J. Exner and M. Bohdanecky, *Chem. Listy.*, **48**, 483 (1959)

22) U. S. Pat. 2, 533, 207 (1950)

23) U. S. Pat. 2, 531, 408 (1950)

24) U. S. Pat. 2, 570, 478 (1951)

25) U. S. Pat. 2, 542, 542 (1951)

26) C. S. Marvel and T. H. Shepherd, *J. Org. Chem.*, **24**, 599 (1959)

27) S. Nagai and K. Yoshida, *Chem. High Polymers* [*Kobunshi-Kagaku*], **17**, 79, 749 (1960)

28) D. Braun and I. A. A. El Sayed, *Makromol. Chem.*, **96**, 100 (1966)

29) T. Sugihara and N. Yoda, *Science and Industry, Japan*, **32**, 217 (1958)

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plotted against the dielectric constant in Fig. 5.

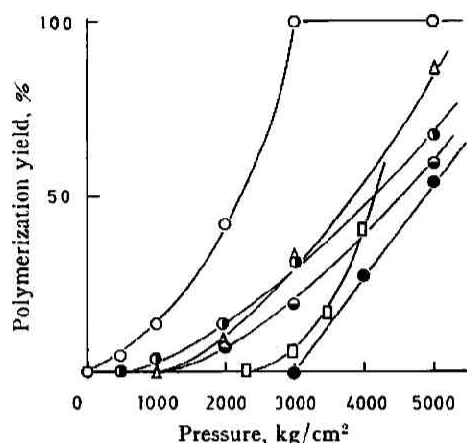


Fig. 4 Polymerization of itaconic acid at high pressure (60°C)

[M]=1.08 mole/l. [I]= 1.43×10^{-2} mole/l.

Polymerization time: 3.0 hr

—○— Dioxane, —□— Tetrahydrofuran,

—◇— Pyridine, —●— Methanol,

—□— Ethanol,

—△— Dimethylformamide

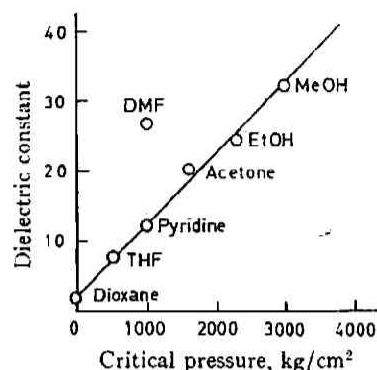


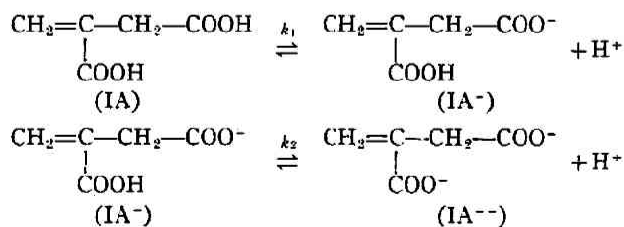
Fig. 5 Effect of dielectric constant on the critical pressure for the polymerization of itaconic acid in different solvents

As shown in Fig. 5 a linear relation between the critical pressure and dielectric constant is obtained. This fact suggests that the possibility to polymerize IA does strongly depend on the nature of the solvent.

Table 5 Critical pressures and dielectric constants in different solvents for the polymerization of itaconic acid (condition see Fig. 4)

Solvent	Dielectric constant	Critical pressure (kg/cm ²)	Solvent	Dielectric constant	Critical pressure (kg/cm ²)
Dioxane	2.21	1	THF	8.2	500
Methanol	32.6	3,000	Ethanol	24.3	2,300
Pyridine	12.3	1,000	Acetone	20.7	1,600
DMF	27	1,000			

Since IA is a weak dibasic acid, it dissociates by two steps in aqueous solution:



According to Nagai and Yoshida the reactivity of (IA⁻) is as same as that of IA while the reactivity of (IA⁻⁻) is much lower than that of (IA⁻).

The dissociation of IA would be markedly dependent upon the nature of solvent, and the degree of the dissociation would generally be larger with increasing dielectric constant of solvent. Therefore, the higher pressure would be required in order to polymerize the acid in a solvent having a higher dielectric constant.

From above consideration, the relation between the dielectric constant and critical pressure would be linear. The ionic complex that may be found between IA and DMF is favourable to the polymerization under high pressure. It is interesting that the critical pressure of DMF agrees with that of pyridine.

The activation volumes of polymerization of IA measured at different temperatures in DMF are shown in Table 6.

Table 6 The activation volumes of itaconic acid at different temperature

Temperature (°C)	40	50	60	70
ΔV^* (ml/mole)	-23.2	-27.4	-30.8	-32.3

The absolute values of the activation volumes indicate fairly large values compared with those of other vinyl polymerization. Since solvation would take place around growing chain because IA considerably dissociates in DMF on account of its large dielectric constant, the large values of the activation volume

Table 7 Results of solution-polymerization of VC in benzene under high pressure

Condition	Composition	VC 3.7 g Benzene 7.4 g AIBN 0.04 g		VC 4.4 g Benzene 6.6 g AIBN 0.05 g	
		Conversion	Degree of polymerization	Conversion	Degree of polymerization
Pressure (kg/cm ²)	Reaction period (hr)	(%)		(%)	
3000	0.5	5.2	—	6.3	517
	1	9.2	367	11.5	455
	2	20.0	384	23.2	455
	3	25.4	419	30.2	493
	5	35.4	367	—	—
	15	59.6	292	—	—
2000	0.5	4.2	—	5.5	438
	1	8.0	368	10.4	437
	2	16.1	311	21.0	419
	3	23.3	384	28.3	367
1000	0.5	3.5	—	4.8	367
	1	6.8	311	9.3	331
	2	13.6	227	19.5	311
	3	20.5	353	27.1	311
1	0.5	2.6	—	3.4	—
	1	6.3	250	7.4	271
	2	12.7	271	16.5	292
	3	18.9	271	24.5	250

would be contributed mainly to the solvation factor.

Polymerization of Vinylchloride³⁰⁾

As it seemed for us that there had been no reports on the polymerization of VC under high pressure, the reaction under the pressure from 1,000 to 3,000 kg/cm² was done in benzene with or without azobisisobutyronitrile as initiator. In Table 7, the conversion and the average degree of polymerization measured by viscometry, of the polymer obtained after 2 hours of reaction period are tabulated for the pressure and feed composition.

With the table it can be recognized that the higher the pressure the higher the polymerization rates are given; for instance the rates at 2,000 kg/cm² and 3,000 kg/cm² become to about 1.27 and 1.58 times to the rate at atmospheric pressure. Although in this table it seems to give lower degree of polymerization than the ordinary commercial PVC polymer, the low values are contributed to the short period of polymerization and not to pressure.

In Table 8 density and degree of crystallinity of the polymer obtained under several pressure and at 3 hours of polymerization period are shown with absorbancy ratio of IR spectra.

Table 8 Pressure effects on density, crystallinity and absorbancy ratio of the polymer

Pressure (kg/cm ²)	Density (g/ml)	Deg. of crystallinity (%)	D_{635}/D_{690}
3,000	1.419	47.9	1.73
2,000	1.411	34.9	1.70
1,000	1.403	21.7	1.66
1	1.397	11.7	1.61

The degree of crystallinity was calculated from the density value measured experimentally by a following relation:

$$\frac{1}{d} = \frac{x_c}{d_c} + \frac{1-x_c}{d_a}$$

where d is density of sample, d_c is density of PVC crystal and equals to 1.452³¹⁾, d_a is density of amorphous part and equals to 1.390 and x_c is the degree of crystallinity of the sample.

The ratio of absorbancy D_{635}/D_{690} of IR spectra is generally considered as a direct measure of syndiotactic structure of PVC polymer. Although from the value of the ratio in Table 8 it can be seen that the proportion of syndiotactic structure increases with pressure, but the increase is not so much as the increase of the degree of crystallinity, x_c . This difference of the rate of increase would be due to the increase of isotactic structure more than the syndiotactic one with pressure.

As a comparison, the density and other properties of PVC polymer obtained by bulk polymerization without solvent are tabulated in Table 9.

30) T. Imoto, Y. Ogo and Y. Hashimoto, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **70**, 1952 (1967)

31) T. Imoto, *Sen-i Gakkai Zasshi*, **13**, 808 (1957)

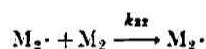
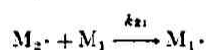
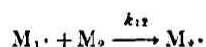
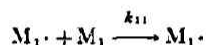
Table 9 Pressure effect on density, crystallinity and absorbandy ratio of PVC obtained by bulk polymerization, mean values of samples polymerized at various reaction periods

Pressure (kg/cm ²)	Deg. of polymerization	Density (g/ml)	Crystallinity (%)	D_{635}/D_{690}
5,000	2,200 ± 200	1.411 ± 0.02	34.9	1.49 ± 0.02
4,000	1,900 ± 200	1.410 ± 0.02	33.2	1.49 ± 0.01
3,000	1,600 ± 200	1.404 ± 0.02	23.4	1.53 ± 0.03

By Table 9 it can be recognized that in spite of higher pressure than in the case of solution-polymerization there are no progressive increase of density, crystallinity and absorbandy ratio in the bulk polymerization, and that the existence of solvent with an adequate quantity would serve to accelerate the isotactic crystallization by the polymerization of VC under high pressure.

Copolymerization of Styrene and Vinylacetate with Vinylchloride³²⁾

In the copolymerization processes of two components monomers, M_1 and M_2 , there are four possible ways in which a monomer can add:



where $M_1 \cdot$ and $M_2 \cdot$ represent chains ending at the M_1 and M_2 monomeric units respectively and where the parameters, $r_1 = k_{11}/k_{12}$ and $r_2 = k_{22}/k_{21}$, are defined as monomer reactivity ratios.

Zutty and Burkhart³³⁾ investigated the copolymerizations of styrene (ST) and acrylonitrile, and of methylmethacrylate and acrylonitrile, under high pressure up to 1,000 kg/cm²; they reported that their individual monomer reactivity ratios increased with the pressure.

On the other hand, the monomer reactivity ratios in the ST-VAc and ST-*n*-butyl vinyl ether systems were found in our previous reports³⁴⁾ not to change with the pressure.

Many investigations of high pressure radical copolymerization have been undertaken in order to explain these disagreement by us^{34)~39)}. And the most reasonable conclusion to be drawn from our available results was that the reactivity ratios of the copolymerization of the nonconjugated vinyl monomer with styrene do not vary with the pressure.

32) T. Imoto, Y. Ogo and H. Nakamoto, *Bull. Chem. Soc. Japan*, **41**, 543 (1968)

33) N. L. Zutty and R. D. Burkhart, *J. Polymer Sci.*, **57**, 793 (1962)

34) T. Imoto and H. Asai, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **85**, 152 (1964)

35) T. Imoto and H. Asai, *ibid.*, **84**, 871 (1963)

36) T. Imoto and H. Asai, *ibid.*, **85**, 155 (1964)

37) T. Imoto and H. Asai, *ibid.*, **85**, 247 (1964)

38) T. Imoto and H. Asai, *ibid.*, **85**, 252 (1964)

39) T. Imoto and H. Asai, *ibid.*, **85**, 312, 347 (1964)

However, the VAc and *n*-butyl vinyl ether used in our previous works are monomers with the lowest reactivity of all the vinyl compounds. Therefore, the constancy of the reactivity ratios in copolymerizations under high pressure may be attributed to their original reactivities. Standing upon these points an attempt was undertaken to determine their effect by means of the copolymerization of VC with a considerable reactivity among various conjugated monomers and ST or VAc.

The monomer-polymer composition curves as experimental data obtained at a 5 per cent total conversion, regardless to the reaction period under each pressure for the two systems, are shown in Fig. 6 and Fig. 7. As these figures show, the copolymer compositions obtained under high pressures form the same line as those at atmosphere, within the experimental error. This fact suggests that the copolymer compositions are quite independent of the pressure for the ST-VC and VC-VAc systems; which means that the monomer reactivity ratios are not affected by the pressure.

The values of r_1 and r_2 evaluated by the Fineman-Ross method are summarized in Table 10.

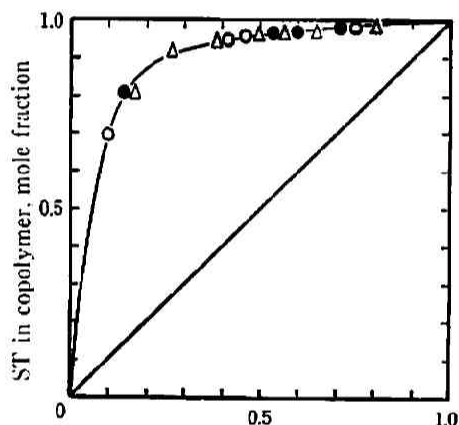


Fig. 6 Copolymer composition curve for ST-VC system (50°C) in acetone

—△—: 3,000 kg/cm²
—○—: 1,000 kg/cm²
—●—: 1 kg/cm²

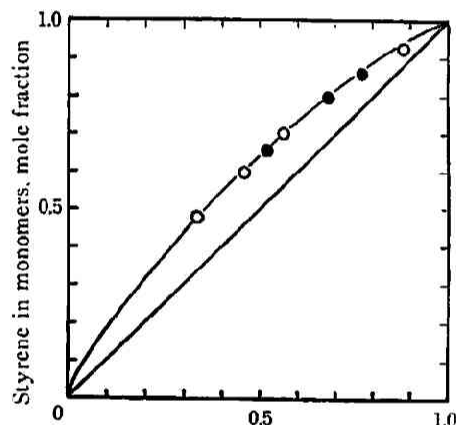


Fig. 7 Copolymer composition curve for VC-VAc system in acetone

—○—: 1,000 kg/cm²
—●—: 1 kg/cm²

Table 10 Monomer reactivity ratios for the system of ST-VC and VC-VAc

System	r_1	r_2
ST-VC	28	0.08
Ham <i>et al.</i> ⁴⁰⁾	40	0.077
VC-VAc	1.60	0.30
Mayo <i>et al.</i> ⁴¹⁾	1.68 ± 0.08	0.23 ± 0.02

These values agree with those obtained by other workers⁴⁰⁾ and show that the ST monomer has a much greater tendency than VC to add either to ST-free radical or to VC-free radical.

40) E. Ham, E. C. Chapin and R. G. Fordyce, *J. Am. Chem. Soc.*, **70**, 538 (1948)

41) F. R. Mayo, C. Walling, F. M. Lewis and W. F. Hulse, *ibid.*, **70**, 1523 (1948)

The results of the high-pressure copolymerization of the ST-VC system lend some support to our previous conclusion about the pressure effect on copolymerization. Moreover, the conclusion may be extended by considering the above results on the VC-VAc system as follows: "the reactivity ratios of the copolymerization between nonconjugated monomers are independent to pressure, and therefore, the pressure effect is available only for the copolymerization of a pair of conjugated monomer".

Copolymerization of Crotonaldehyde with Various Vinyl Compounds^{42,43)}

There are two functional groups in the unsaturated compound with carbonyl for polymerization, such as crotonaldehyde (CA); namely aldehyde group and double bond group. The problem, which group does attribute to its polymerization, will get different answers according to the polymerization conditions, especially the kind of initiator and comonomer in the case of copolymerization. Thus, the behavior of such CA in polymerization and/or copolymerization must be interesting, however, seldom reports on this theme have been presented. In addition, the CA can be easily produced in a large scale from acetaldehyde and are abundant. On these views, we have been studying on the polymerization and copolymerization of CA under high pressure. In follows some results of the copolymerization with various vinyl compounds will be briefly summarized.

Copolymerization with Styrene

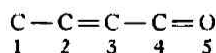
High pressure copolymerization of ST and CA in bulk (therefore out of scope for this article concerning to solvent effect) at 100°C under 1~1,000 kg/cm² was investigated. The monomer reactivity ratios, r_1 and r_2 , were calculated by the Fineman-Ross method as shown in Table 11, where suffices 1 and 2 denote ST and AC respectively.

Table 11 Pressure effect on copolymerization of ST and CA

Pressure (kg/cm ²)	r_1	r_2	$r_1 \cdot r_2$
1	14.7	0.03	0.441
500	14.7	0.07	1.029
1000	14.7	0.12	1.764

As seen in this table, r_2 increased with the increase of pressure, but r_1 was not affected by pressure. Accordingly, the product $r_1 \cdot r_2$ increased with pressure to values over 1 which was unexpected phenomena by Zutty and Burkhart³³⁾ who formerly assumed that the product value must increase to one with pressure, signifying an approach to the perfect copolymerization.

In the infrared spectra (omitted here) of the copolymer obtained, there can be found each characteristic absorptions of CH₃ in 1385 cm⁻¹, C=O in 1720 cm⁻¹ and CH in 2720 cm⁻¹, respectively. If the backbone structure of CA is designated as



42) T. Imoto, Y. Ogo, S. Goto and T. Mitani, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **69**, 1371 (1966)

43) T. Imoto, Y. Ogo and T. Mitani, *ibid.*, **70**, 1217 (1967)

the 2-3 addition, 2-5 addition and 4-5 addition could be considered as the elementary reaction of the copolymerization. But since any absorption spectra of ether linkage or double bond in the IR chart, it seems reasonable to assume that only 2-3 addition is the plausible reaction and that the product is a copolymer having pendant carbonyl groups.

Copolymerization with acrylonitrile

As described in the previous section of this article, if the conclusion that the pressure affects the copolymerization of a pair of conjugated monomer is true, the copolymerization of CA and acrylonitrile (AN) must be affected considerably by the pressure, because the structure of these comonomers are conjugative. But, as shown in Figs. 8 and 9, the copolymer compositions were quite independent not only of the pressure but also of the existence of solvent (DMF). In this case some other causes should be attributed.

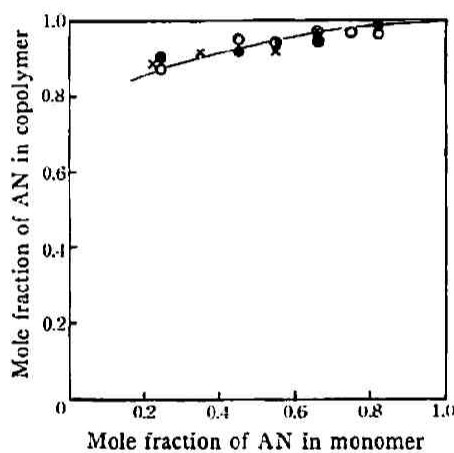


Fig. 8 Curve of copolymer composition in solution and with initiator

—○—: 1,000 kg/cm²
—●—: 500 kg/cm²
—×—: 1 kg/cm²

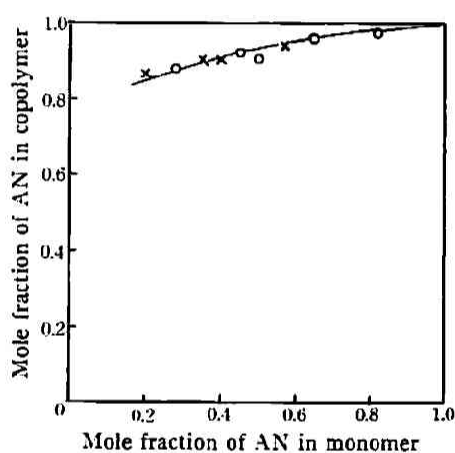


Fig. 9 Curve of copolymerization composition in bulk and without initiator

—○—: 1,000 kg/cm²
—×—: 1 kg/cm²

Generally speaking, chemical structural effect of comonomer upon the behavior of copolymerization can be divided into three kinds: (a) steric effect, (b) polar effect and (c) resonance stability. Comparing the AN with ST as comonomer towards CA, there is no significant difference between ST and AN about the steric effect, in spite of the increase of r_2 value in the case of ST as described in the former section. Moreover, since there is no dependency to the existence of solvent in the case of AN, the polar effect upon the copolymerization of CA may be neglected for both AN and ST. Therefore only the last effect, resonance stability of radical formed, should differ between AN and ST.

According to Walling⁴⁴⁾, the increase of the resonance stability owing to substituent Y of olefinic monomer $\text{CH}_2=\text{CHY}$ is to be in the following order.



44) C. Walling, "Free Radicals in Solution", John Wiley (1957)

Thus ST has a higher stability of resonance than AN. And also Walling suggested that the higher the stability of monomer the larger the pressure effect upon the copolymerization could be expected. After all, it can be assumed according to Walling's theorem that the pressure independency to the r -values of CA-AN system should be originated to the low resonance stability of AN.

In addition, it is suspected also from the IR spectra of the copolymer obtained that the reasonable reaction of CA for this case may be the 2-3 addition which can be detected by a reaction of 2,4-dinitrophenylhydrazine with the pendant carbonyl groups in the copolymer formed.

Copolymerization with other olefinic monomers

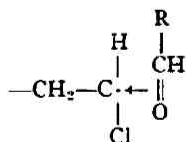
For the comparison, various olefinic monomers, like as VC, methylacrylate, methylmetacrylate, VAc, α -methylstyrene, n -butylvinylether and acrylamide, were submitted to the copolymerization with CA under high pressure up to 1,000 kg/cm². The results as pressure effects are summarized in Table 12 diagrammatically including the case of ST and AN.

Table 12 Pressure effect to copolymerization of CA with olefinic monomers in the presence of AIBN

Monomer	Ability of homopolymerization	Ability of copolymerization	Changeability of composition of copolymer
styrene		+	+
acrylonitrile		+	-
vinylchloride		slightly -	
methylacrylate		slightly +	
methylmetacrylate	+	-	
vinylacetate	-	-	
α -methylstyrene	-	-	
n -butylvinylether	-	-	
acrylamide	-	-	

In the above table, + shows the acceleration ability of the pressure for copolymerization and homopolymerization and - indicates the independency to the pressure. For instance, methylmetacrylate does not copolymerize with CA, but homopolymerize alone in spite of existence of CA. VAc does neither copolymerize in the presence of CA, because CA may serve as an inhibitor.

As shown in the table, the monomers which can easily copolymerize with CA are only ST and AN. Methylacrylate can copolymerize with CA slightly in trace. The copolymerization of CA and VC is contrariwise depressed by the pressure. This fact would be due to the following complex formation between VC and aldehyde group as suggested by Burleigh⁴⁵⁾,



VAc, α -methylstyrene, n -butylvinylether and acrylamide do neither copolymerize nor homopolymerize even under high pressure owing to steric effect, may be.

45) P. H. Burleigh *et al.*, *J. Polymer Sci.*, 54, 31 (1961)

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